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Solid-Liquid Equilibria of Some Natural Phenolic Compounds: Experimental and Modelling

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Introduction

Phenolic compounds are typically found in plants, usually as esters or glycosides [1]. Apart from being starting materials for many chemical synthesis, there is also huge evidence that some phenolic compounds have beneficial effects on human health.

In this work, the aqueous solubilities of some phenolic compounds such as the hydroxybenzoic acids gallic, salicylic, protocatechuic and syringic acids, and the phenilpropenoic acids caffeic, cinnamic, ferulic and coumaric acids are addressed. Measurements were performed, as a function of temperature, between 288 K and 323 K, at atmospheric pressure, using constant-temperature jacketed equilibrium glass cells.

Approaches for modelling the measured data were evaluated, including the modified UNIQUAC model [2] and the CPA equation of state [3].

Experimental

Solubility measurements were carried out using the analytical shake-flask method. Excess solute and 200 mL of bidistilled water were introduced into the cells and stirred in a plate stirrer. Temperature was controlled with a constant-temperature circulating water bath. For the determination of solubilities, liquid samples were taken using plastic syringes coupled with filters. Compositions of the saturated aqueous phases were obtained by spectrophotometry.

The pH of the saturated aqueous solutions and the apparent acid dissociation constants of the phenolic acids were determined by potentiometry with a glass electrode.

Differential scanning calorimetry was used to obtain thermograms of the pure phenolics. Samples of about 4-6 mg were sealed hermetically into aluminium crucibles and heated under a stream of nitrogen. Between 3 and 5 runs were averaged with a heating rate of 1K/min around the expected melting temperature.

Modelling

An activity coefficient model, the modified UNIQUAC [2] and an equation of state, the CPA EoS [3] were evaluated for modelling the measured data.

The modified UNIQUAC model consists of two terms: a combinatorial term, that attempts to describe the dominant entropic contribution and a residual term to account for the intermolecular forces responsible for the enthalpy of mixing. The modified UNIQUAC model proposed by Peres and Macedo [2] was used in this work.

As both the solutes and the solvent (water) can associate (self and cross-association is present in these mixtures), the CPA EoS was also adopted in this work. As the studied phenolic acids are multifunctional associating molecules a new methodology was proposed to take into account the different associating groups as well as their repetitions and ring positions in the chemical structure.

The general solid-liquid equilibria relation was employed [4], neglecting the heat capacity term.

Results and discussion

Figure 1 shows the measured solubility data of some studied phenolic compounds as well as the modelling results obtained with UNIQUAC and CPA.

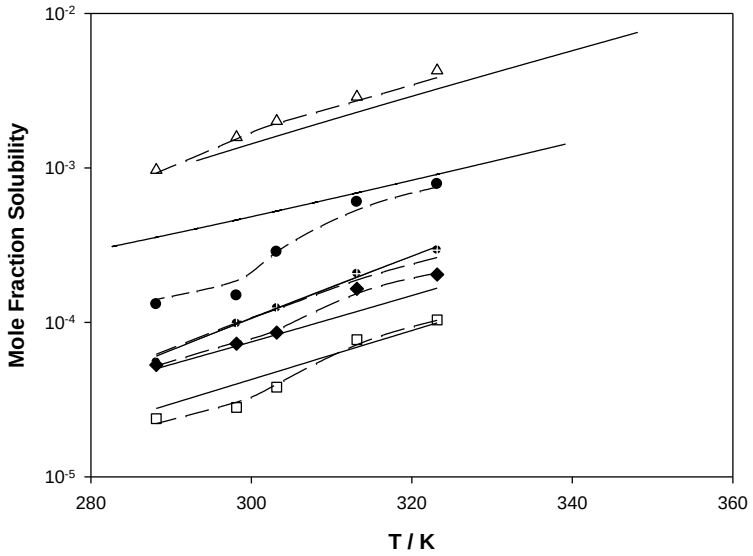

Figure 1: Experimental solubility data (●, salicylic acid; Δ, gallic acid; □, trans-cinnamic acid; crossed circles, caffeic acid; ♦, ferulic acid) and modelling results by CPA (solid line) and UNIQUAC (dotted line).

Among the hydroxybenzoic acids, gallic acid has the higher solubilities due to the higher number of hydroxyl groups, leading to increased association interactions with water. In the series of phenilpropenoic compounds, higher solubilities for caffeic, followed by ferulic and trans-cinnamic acid were obtained. Also, this order follows the extent of hydrogen bonding of each molecule with water, as caffeic acid has two hydroxyl groups, ferulic one, and cinnamic acid none. Both models proof to be adequate tools for the description of the solid solubility of phenolic compounds.

Because of the aromatic ring, the hydrogen of the phenolic hydroxyl is labile, which makes phenols weak acids. From the measured pKa values it was found that hydroxybenzoic acids are more acidic than phenilpropenoic acids, with salicylic acid, the less soluble, being the most acidic of all the studied compounds. Among the phenilpropenoic acids, the less soluble *trans*-cinnamic acid is the most acidic.

From the measured melting data, pKa and solubility data, it can be concluded that the extent of hydrogen bonding with water is the dominant effect in determining the degree of solubilization.

Conclusion

In this work, aqueous solubility data were measured for some phenolic compounds, in pure water, in the temperature range from 288 K to 323 K, by the shake-flask method coupled with spectrophotometric analysis. For all compounds, the solubility follows the general increasing trend with temperature. Besides solubility data, melting data and apparent acid dissociation constants were also determined, providing a broader knowledge about the solubilization processes of these molecules. Both CPA EoS and modified UNIQUAC model showed to be appropriate tools to represent the water solubility of these molecules.

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